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**Blatt 2 der Bescheinigung**  
**Sheet 2 of the certificate**  
**Page 2 de l'attestation**

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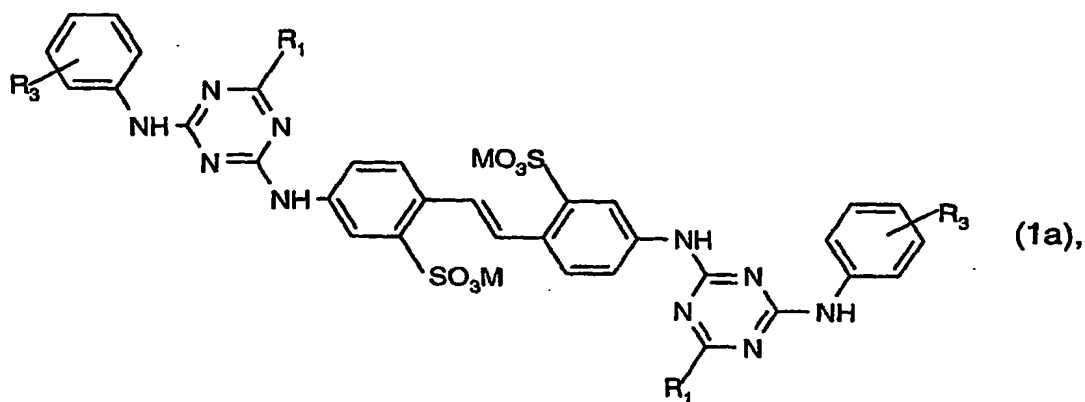
Triazinylaminostilbene Disulphonic Acid Mixtures

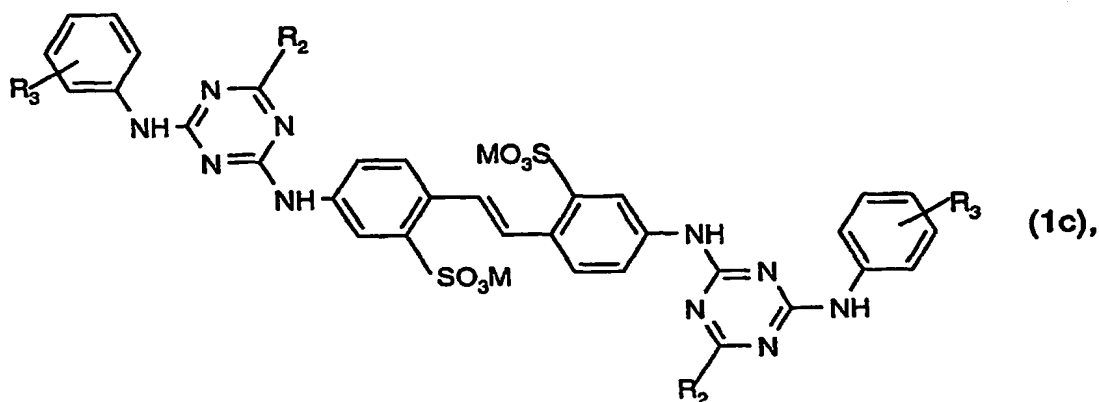
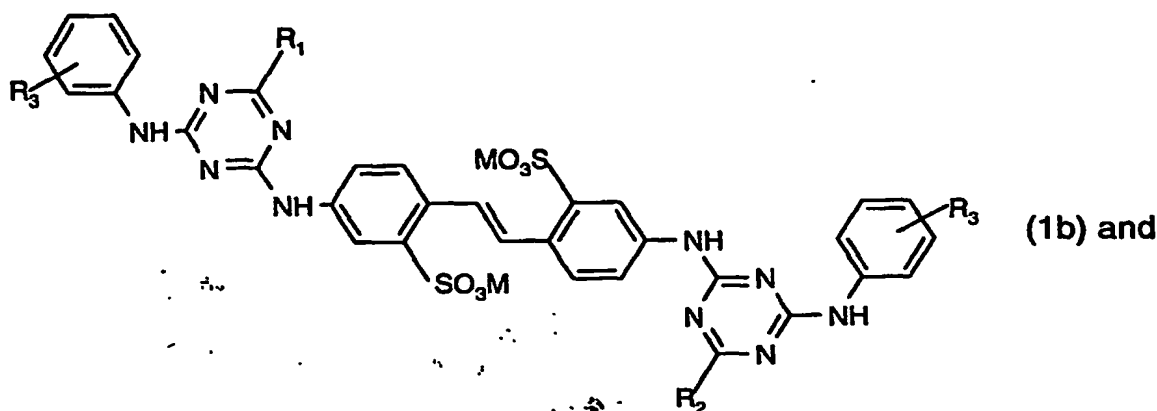
The present invention relates to a fluorescent whitening agent comprising a mixture of two symmetrically and one unsymmetrically substituted triazinylaminostilbene disulphonic acids, novel unsymmetrically substituted derivatives, a process for their preparations and use of the mixture for whitening synthetic or natural organic materials, especially paper.

Mixtures of triazinylaminostilbene sulphonic acids for whitening paper have been disclosed in US 3,132,106. However such mixtures are restricted to the tetrasulphonic acids, which are especially suitable for whitening paper in pulp applications and less desirable for present day whitening techniques such as coating or size-press applications.

Surprisingly, it has now been found that mixtures of triazinylaminostilbene disulphonic acids are eminently suitable for use, not only in pulp applications, but also in paper coating and size-press applications, where they exhibit extremely high degrees of whiteness and, furthermore, may be readily formulated as stable liquid compositions.

Accordingly, the present invention relates to a fluorescent whitening agent, which comprises a mixture of compounds of the formulae





in which

$\text{R}_1$  and  $\text{R}_2$  are different and each represents  $-\text{NH}_2$ ,  $-\text{NHC}_1\text{-C}_4\text{alkyl}$ ,  $-\text{N}(\text{C}_1\text{-C}_4\text{alkyl})_2$ ,  $-\text{NHC}_2\text{-C}_4\text{hydroxyalkyl}$ ,  $-\text{N}(\text{C}_2\text{-C}_4\text{hydroxyalkyl})_2$ ,  $-\text{N}(\text{C}_1\text{-C}_4\text{alkyl})(\text{C}_2\text{-C}_4\text{hydroxyalkyl})$ , a morpholino, piperidino or pyrrolidino residue or an amino acid or an amino acid amide residue from which a hydrogen has been removed from the amino group, each  $\text{R}_3$ , independently, represents hydrogen,  $\text{C}_1\text{-C}_4\text{alkyl}$  or  $\text{C}_1\text{-C}_4\text{alkoxy}$  and  $\text{M}$  represents hydrogen, an alkali metal atom, ammonium or a cation formed from an amine, whereby  $\text{R}_3$  preferably represents hydrogen.

When  $\text{R}_1$  and/or  $\text{R}_2$  represent an amino acid or amino acid amide residue, this is preferably of the formula



in which each

$\text{R}_4$  and  $\text{R}_4'$ , independently, represent hydrogen or a group having the formula  $-\text{CHR}_5\text{R}_6$  in which

$R_5$  and  $R_6$ , independently, are hydrogen or  $C_1$ - $C_4$ alkyl optionally substituted by one or two substituents selected from the group consisting of hydroxy, thio, methylthio, amino, carboxy, sulfo, phenyl, 4-hydroxyphenyl, 3,5-diiodo-4-hydroxyphenyl,  $\beta$ -indolyl,  $\beta$ -imidazolyl and  $NH=C(NH_2)NH$ .

More preferably, the residues  $R_1$  and/or  $R_2$  are derived from glycine, alanine, sarcosine, serine, cysteine, phenylalanine, tyrosine (4-hydroxyphenylalanine), diiodotyrosine, tryptophan ( $\beta$ -indolylalanine), histidine ( $\beta$ -imidazolylalanine),  $\alpha$ -aminobutyric acid, methionine, valine ( $\alpha$ -aminoisovaleric acid), norvaline, leucine ( $\alpha$ -aminoisocaproic acid), isoleucine ( $\alpha$ -amino- $\beta$ -methylvaleric acid), norleucine ( $\alpha$ -amino-n-caproic acid), arginine, ornithine ( $\alpha,\delta$ -diaminovaleric acid), lysine ( $\alpha,\epsilon$ -diaminocaproic acid), aspartic acid (aminosuccinic acid), glutamic acid ( $\alpha$ -aminoglutaric acid), threonine, hydroxyglutamic acid and taurine, as well as mixtures and optical isomers thereof, or from iminodiacetic acid or from N-(propionamido)-N-(2-hydroxyethyl)amine.

Most preferably, however,  $R_1$  and/or  $R_2$  represent  $-NHC_2$ - $C_4$ hydroxyalkyl,  $-N(C_2$ - $C_4$ hydroxyalkyl) $_2$ ,  $-N(C_1$ - $C_4$ alkyl)( $C_2$ - $C_4$ hydroxyalkyl), a morpholino residue or a residue derived from glycine, sarcosine, taurine, glutamic acid, aspartic acid or iminodiacetic acid and, especially,  $R_1$  and  $R_2$  represent a diethanolamino, a di-(2-hydroxypropyl)amino, an N-(2-hydroxyethyl)-N-methylamino, an aspartic acid, iminodiacetic acid or a morpholino residue.

In the compounds of formulae (1a) - (1c), M represents hydrogen, lithium, potassium, sodium, ammonium, mono-, di-, tri- or tetra- $C_1$ - $C_4$ alkylammonium, mono-, di- or tri- $C_1$ - $C_4$ hydroxyalkylammonium or ammonium that is di- or tri-substituted with a mixture of  $C_1$ - $C_4$ alkyl and  $C_1$ - $C_4$ hydroxyalkyl groups, i.e.  $H_2N^+(C_1$ - $C_4$ alkyl)( $C_1$ - $C_4$ hydroxyalkyl) and  $HN^+(C_1$ - $C_4$ alkyl) $_m$ ( $C_1$ - $C_4$ hydroxyalkyl) $_n$ , where n and m represent 1 or 2, but preferably M represents hydrogen, potassium or sodium.

In a most preferred aspect, the invention relates to a fluorescent whitening agent comprising a mixture of the compounds of formulae (1a), (1b) and (1c) in which  $R_1$  represents diethanolamino,  $R_2$  represents di-(2-hydroxypropyl)amino, an aspartic acid or iminodiacetic acid residue  $R_3$  represents hydrogen and M represents sodium.

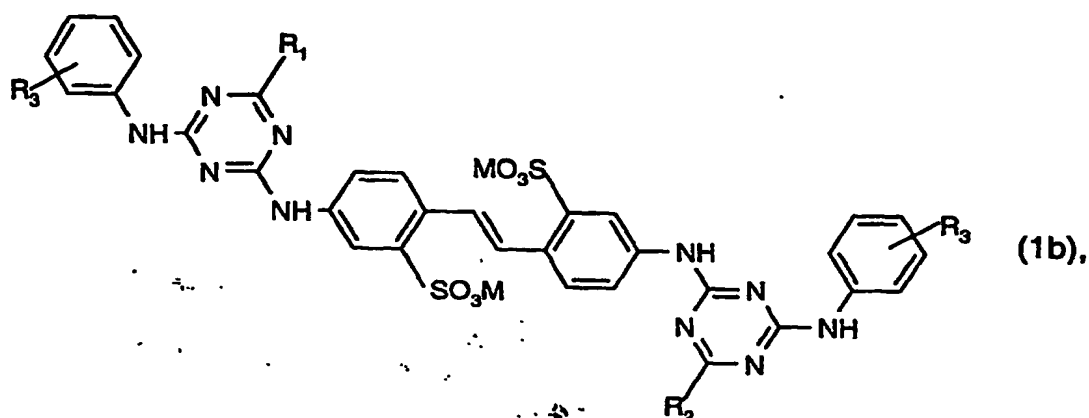
Where  $R_1$ ,  $R_2$  and/or  $R_3$  contain  $C_1$ - $C_4$ alkyl radicals, these may be branched or unbranched and are, for example, methyl, ethyl, n-propyl, isopropyl or n-butyl; isobutyl or tet.-butyl, whilst

C<sub>1</sub>-C<sub>4</sub>alkoxy is, for example, methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy or tert.-butoxy. C<sub>1</sub>-C<sub>4</sub>hydroxyalkyl may, for example, be hydroxymethyl, hydroxyethyl, hydroxypropyl or hydroxybutyl.

The compound mixture of formulae (1a), (1b) and (1c) may be prepared by reacting, under known reaction conditions, cyanuric chloride, successively, in any desired sequence, with each of 4,4'-diaminostilbene-2,2'-disulphonic acid, aniline or a derivative thereof, an amino compound R<sub>1</sub>H and an amino compound R<sub>2</sub>H, or, alternatively a mixture of amino compounds R<sub>1</sub>H and R<sub>2</sub>H, R<sub>1</sub> and R<sub>2</sub> being as defined previously. However, preferably, cyanuric chloride is initially reacted with 4,4'-diaminostilbene-2,2'-disulphonic acid, followed by reaction with aniline or alkyl or alkoxy derivatives thereof and, finally, with a mixture of amino compounds R<sub>1</sub>H and R<sub>2</sub>H.

Depending on the amounts and proportions of the amines R<sub>1</sub>H and R<sub>2</sub>H and whether they are added sequentially or simultaneously as a mixture, the proportions of the compounds (1a), (1b) and (1c) can be varied considerably. Thus, the present invention relates to a fluorescent whitening agent which comprises a mixture of the compounds (1a), (1b) and (1c) wherein each of the components are present in a molar ratio of between 5 and 80%, preferably they are present in the approximate molar ratios of 5-45% of the compound of formula (1a), 15-60% of the compound of formula (1b) and 5-45% of the compound of formula (1c). More preferably, the compounds (1a), (1b) and (1c) are present in the approximate molar ratios of 20-50% of the compound of formula (1a), 25-50% of the compound of formula (1b) and 5-35% of the compound of formula (1c).

Naturally, such compositions may also be obtained simply by mechanical mixing of the individual components in the desired proportions. In this case it is necessary to obtain the individual components as pure substances. Whilst the components of formulae (1a) and (1c) are known compounds or may be prepared by known methods, compounds of formula (1b) are new. Consequently, a further aspect of the invention is a compound of formula



in which

$R_1$ ,  $R_2$ ,  $R_3$  and  $M$  are as defined previously.

The compound of formula (1b) may either be obtained by purification of the mixture obtained as described above, or, for example, by the following reaction sequence:

- i) Reaction of cyanuric chloride with 4-amino-4'-nitrostilbene-2,2'-disulphonic acid with cyanuric chloride;
- ii) reaction of the dichloro intermediate with aniline or an aniline derivative;
- iii) reaction of the monochloro intermediate with an amine  $R_1H$  or  $R_2H$ ;
- iv) reduction of the nitrostilbene to the aminostilbene;
- v) reaction with cyanuric chloride;
- vi) reaction of the dichloro intermediate with aniline or an aniline derivative and
- vii) reaction of the monochloro intermediate with an amine  $R_2H$  or  $R_1H$ .

Naturally, this reaction sequence may be performed in any desirable and practical order.

A further aspect of the invention is the use of a composition for whitening synthetic or natural organic materials, which contains water, a fluorescent whitening agent which comprises a mixture of the compounds (1a), (1b) and (1c) and, optionally, auxiliaries.

More specifically, such brightener compositions contain water and, in each case based on the weight of the formulation, from 3 to 25% by weight, preferably from 5 to 15% by weight of the above defined fluorescent whitening agent mixture and also 0 to 60%, preferably 5 to 50% by weight, of auxiliaries.

Suitable auxiliaries include, for example, anionic or non-ionic dispersants from the class of ethylene oxide adducts with fatty alcohols, higher fatty acids or alkyl phenols or ethylenediamine ethylene oxide-propylene oxide adducts, copolymers of N-vinylpyrrolidone with 3-vinylpropionic acid, water retention aids, such as ethylene glycol, glycerol or sorbitol, or biocides.

Most of the compositions comprising a mixture of the compounds of formulae (1a), (1b) and (1c) are excellent fluorescent whitening agents for substrates such as textiles, for the addition to detergent compositions and, especially for the fluorescent whitening of paper.

When used for the fluorescent whitening of paper, the composition, which contains water, a fluorescent whitening agent which comprises a mixture of the compounds (1a), (1b) and (1c) and, optionally, auxiliaries, may be applied to the paper substrate in the pulp mass, in the form of a paper coating composition, or directly in the size press or metering press.

In one preferred aspect, the present invention provides a method for the fluorescent whitening of a paper surface, comprising contacting the paper surface with a coating composition comprising a white pigment; a binder dispersion; optionally a water-soluble co-binder; and sufficient of a fluorescent whitening agent comprising a mixture of the compounds of formulae (1a), (1b) and (1c) according to the present invention, to ensure that the treated paper contains 0.01 to 1 % by weight, based on the white pigment, a fluorescent whitening agent.

As the white pigment component of the paper coating composition used according to the method of the present invention, there are preferred inorganic pigments, e.g., aluminium or magnesium silicates, such as China clay and kaolin and, further, barium sulfate, satin white, titanium dioxide, calcium carbonate (chalk) or talcum; as well as white organic pigments.

The paper coating compositions used according to the method of the present invention may contain, as binder, inter alia, plastics dispersions based on copolymers of butadiene/styrene, acrylonitrile/butadiene/styrene, acrylic acid esters, acrylic acid esters/styrene/acrylonitrile, ethylene/vinyl chloride and ethylene/vinyl acetate; or homopolymers, such as polyvinyl chloride, polyvinylidene



chloride, polyethylene and polyvinyl acetate or polyurethanes. A preferred binder consists of styrene/butyl acrylate or styrene/butadiene/ acrylic acid copolymers or styrene/butadiene rubbers. Other polymer latices are described, for example, in U.S. Patent Specifications 3,265,654, 3,657,174, 3,547,899 and 3,240,740.

The optional water-soluble protective colloid may be, e.g., soya protein, casein, carboxymethylcellulose, natural or modified starch, chitosan or a derivative thereof or, especially, polyvinyl alcohol. The preferred polyvinyl alcohol protective colloid component may have a wide range of saponification levels and molecular weights; e.g. a saponification level ranging from 40 to 100; and an average molecular weight ranging from 10,000 to 100,000.

Recipes for coating compositions for paper are described, for example, in J.P. Casey "Pulp and Paper"; Chemistry and Chemical Technology, 2nd edition, Volume III, pages 1684-1649 and in "Pulp and Paper Manufacture", 2nd and 5th edition, Volume II, page 497 (McGraw-Hill).

The paper coating compositions used according to the method of the present invention preferably contain 10 to 70% by weight of a white pigment. The binder is preferably used in an amount which is sufficient to make the dry content of polymeric compound up to 1 to 30% by weight, preferably 5 to 25% by weight, of the white pigment. The amount of fluorescent brightener preparation used according to the invention is calculated so that the fluorescent brightener is preferably present in amounts of 0.01 to 1% by weight, more preferably 0.05 to 1% by weight, and especially 0.05 to 0.6% by weight, based on the white pigment.

The paper coating composition used in the method according to the invention can be prepared by mixing the components in any desired sequence at temperature from 10 to 100°C, preferably 20 to 80°C. The components here also include the customary auxiliaries, which can be added to regulate the rheological properties, such as viscosity or water retention capacity, of the coating compositions. Such auxiliaries are, for example, natural binders, such as starch, casein, protein or gelatin, cellulose ethers, such as carboxyalkylcellulose or hydroxyalkylcellulose, alginic acid, alginates, polyethylene oxide or polyethylene oxide alkyl ethers,

copolymers of ethylene oxide and propylene oxide, polyvinyl alcohol, water-soluble condensation products of formaldehyde with urea or melamine, polyphosphates or polyacrylic acid salts.

The coating composition used according to the method of the present invention is preferably used to produce coated printed or writing paper, or special papers such as ink-jet or photographic papers, or cardboard.

The coating composition used according to the method of the invention can be applied to the substrate by any conventional process, for example with an air blade, a coating blade, a roller, a doctor blade or a rod, or in the size press, after which the coatings are dried at paper surface temperatures in the range from 70 to 200°C, preferably 90 to 130°C, to a residual moisture content of 3-8%, for example with infra-red driers and/or hot-air driers. Comparably high degrees of whiteness are thus achieved even at low drying temperatures.

By the use of the method according to the invention, the coatings obtained are distinguished by optimum distribution of the dispersion fluorescent brightener over the entire surface and by an increase in the level of whiteness thereby achieved, by a high fastness to light and to elevated temperature (e.g. stability for 24 hours at 60-100°C.) and excellent bleed-fastness to water.

In a second preferred aspect, the present invention provides a method for the fluorescent whitening of a paper surface comprising contacting the paper in the size press with an aqueous solution containing a size, optionally an inorganic or organic pigment and 0.1 to 20g/l of a fluorescent whitening agent comprising a mixture of the compounds of formulae (1a), (1b) and (1c) according to the present invention. Preferably, the size is starch, a starch derivative or a synthetic sizing agent, especially a water-soluble copolymer.

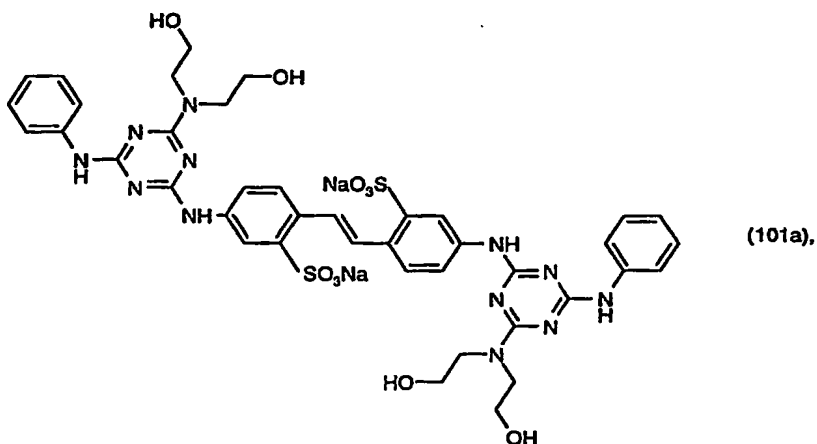
The fluorescent whitening agents of the present invention are particularly advantageous in that they exhibit not only extremely high whitening ability, excellent substantivity and fastness properties, but, in addition, in many cases highly desirable water solubilities, thus enabling ready preparation of stable concentrated liquid formulations.

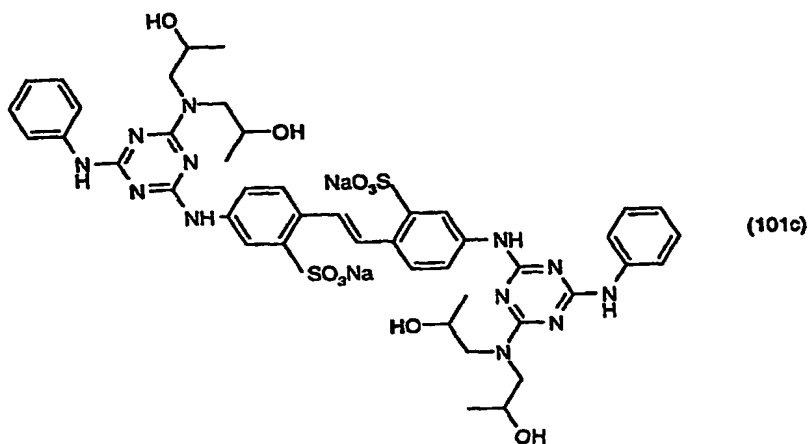
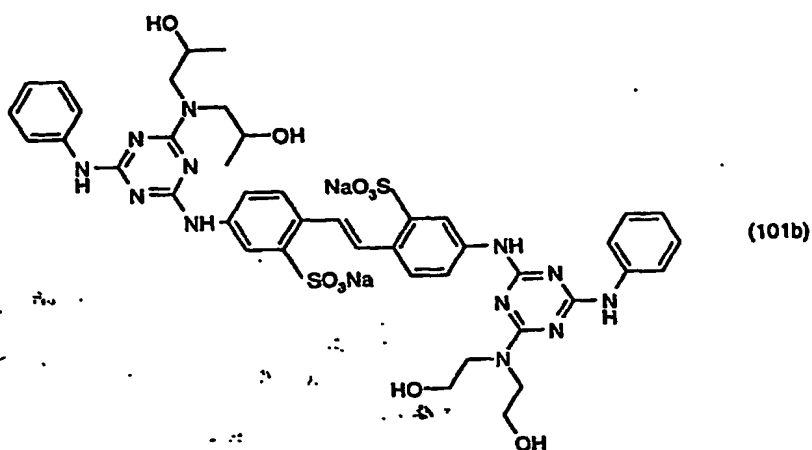
The following Examples serve to illustrate the invention without intending to be restrictive in nature; parts and percentages are by weight, unless otherwise stated.

### Preparative Examples

#### Example 1

11.0g of 4,4'-bis [(4-anilino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid disodium salt are stirred in 120ml of water. To the resulting suspension, 1.64g of diethanolamine and 2.07g of di-isopropanolamine are added. The mixture is then heated to 95°C and stirred for 3 hours at this temperature, the pH being maintained at 8.0-8.5 by addition of a total of 3.0g of 32% aqueous sodium hydroxide solution. The mixture is then cooled during which time two phases separate. The lower phase is separated off, diluted with 50ml of acetone and acidified to pH 4-5 by addition of 4N aqueous hydrochloric acid. The precipitated solids are filtered and washed with water. The filter-cake is stirred in water and the pH adjusted to 10 by addition of 2N aqueous sodium hydroxide solution, when a clear solution results. The water is evaporated off and the residue dried under vacuum at 80°C to yield the fluorescent whitening agent (101), which comprises a mixture containing 41% of the compound (101a), 26% of compound (101b) and 24% compound (101c), in addition to 4.5% water and 0.5% sodium chloride.





### Example 2

By proceeding as described in Example 1, but employing 1.76g of diethanolamine and 1.60g of di-isopropanolamine, the fluorescent whitening agent (102) is obtained, which comprises a mixture containing 42% of compound (101a), 44.5% of compound (101b) and 6.5% of compound (101c), together with 2% water and 0.07% sodium chloride.

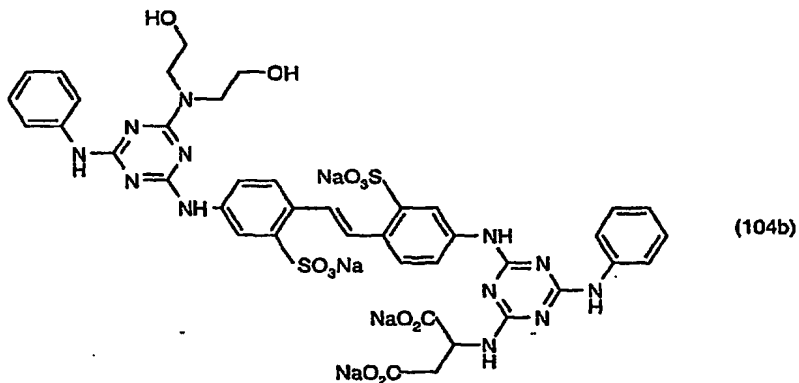
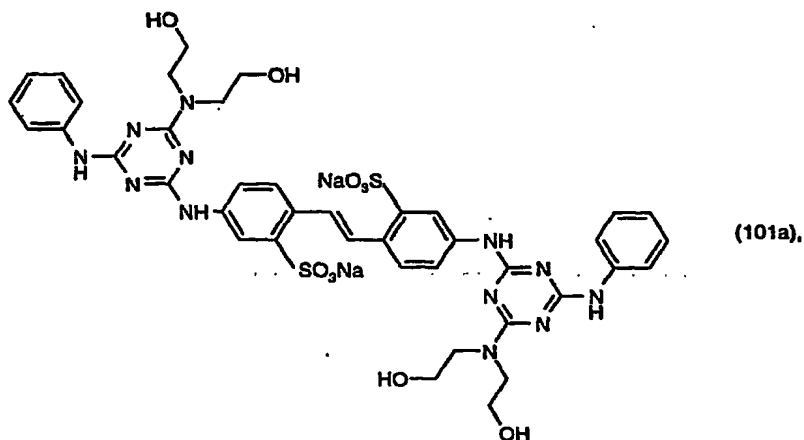
### Example 3

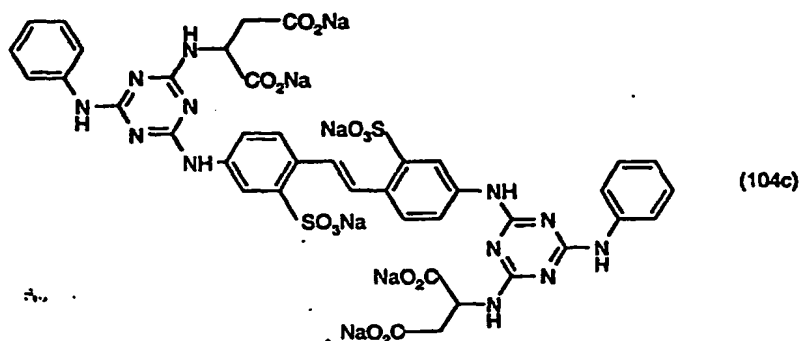
By proceeding as described in Example 2, but by working up the entire reaction mass, instead of phase separation, by acidification with 4N hydrochloric acid to pH 4, addition of 50ml of acetone, filtering the solids, dissolution in water and 32% aqueous sodium hydroxide solution, evaporation of the water and drying the product at 80°C under vacuum, a fluorescent whitening agent (103) is obtained, which comprises a mixture containing 32.5%

of compound (101a), 44.5% of compound (101b) and 14.5% of compound (101c), together with 3.5% water and 0.03% sodium chloride.

Example 4

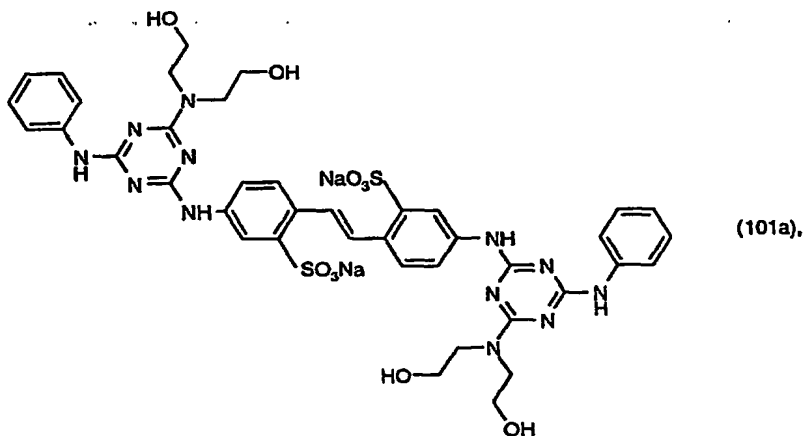
15.0g of 4,4'-bis [(4-anilino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid disodium salt are suspended in 14.0g of polyethylene glycol 300 and 29.6g of water. To the stirred suspension are then added 2.15g of aspartic acid, 1.7g of diethanolamine and 1.2g of 50% aqueous sodium hydroxide solution. The reaction mixture is heated to 90°C and stirring continued at this temperature for 7 hours, the pH being maintained at 8.5-9.3 by addition of 32% aqueous sodium hydroxide solution. The reaction mixture is cooled and filtered to yield a liquid formulation containing 24.6% of the fluorescent whitening agent (104), which comprises a mixture containing 39% of compound (101a), 22% of compound (104b) and 33% of compound (104c).

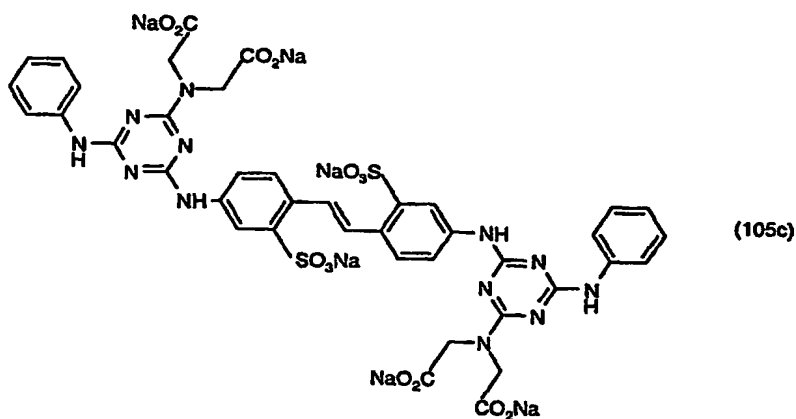
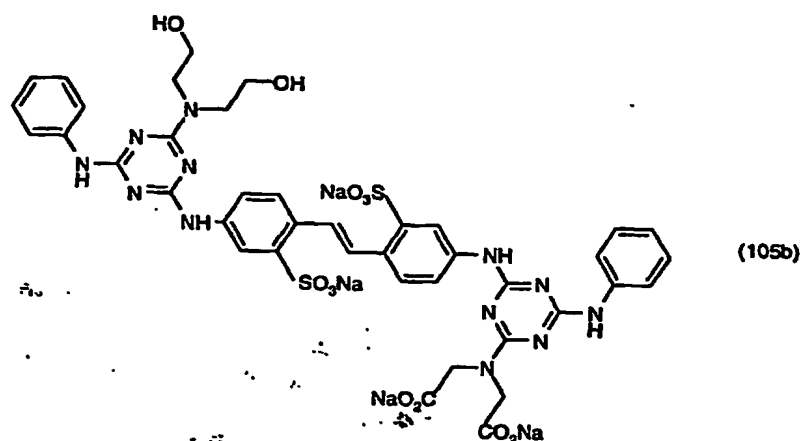




### Example 5

30.0g of 4,4'-bis [(4-anilino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid disodium salt are suspended in 28.0g of polyethylene glycol 300 and 58.0g of water. To the stirred suspension are then added 4.26g of iminodiacetic acid and 3.37g of diethanolamine. The reaction mixture is heated to 95°C and stirring continued at this temperature for 7 hours, the pH being initially adjusted to 8.5-9.0 by addition of 5.07g of 50% aqueous sodium hydroxide solution and maintained at this value by addition of 7.8g of 32% aqueous sodium hydroxide solution. The reaction mixture is cooled and filtered to yield a liquid formulation containing 25% of the fluorescent whitening agent (105), which comprises a mixture of 28% of compound (101a), 44% of compound (105b) and 26% of compound (105c).





#### Example 6 – Synthesis of Compound (104b)

##### *Step 1.*

To a stirred suspension of 9.8g of cyanuric chloride in 100g of ice-water and 50ml of acetone is added a mixture of 25g of 84.9% 4-amino-4'-nitrostilbene-2,2'-disulphonic acid. After the addition, stirring is continued for 40 minutes at 5°C, the pH being maintained at 4.0-4.5 by addition of a total amount of approximately 60ml of 1M aqueous sodium carbonate solution. After this time, 4.93g of aniline are added and the mixture heated to 50 °C, the pH being maintained at 6.5-7.0 by addition of a total amount of 28ml of 1M aqueous sodium carbonate solution. To the resulting suspension, 7.25g of diethanolamine in 30ml of water are added and the temperature raised to 95°C, the acetone being distilled off and the pH being maintained at 7.5-8.0 by addition of a total amount of approximately 20ml of 1M aqueous sodium carbonate solution. After cooling, the pH is adjusted to 3.0 by addition of 6N aqueous hydrochloric acid solution and the precipitated solids filtered and dried under vacuum at 80°C

to yield 4-[(4-anilino-6-diethanolamino-1,3,5-triazin-2-yl)amino]-4'-nitrostilbene-2,2'-disulphonic acid.

*Step 2*

0.02 Moles of 4-[(4-anilino-6-diethanolamino-1,3,5-triazin-2-yl)amino]-4'-nitrostilbene-2,2'-disulphonic acid are reduced with 0.3 moles of iron filings and 11g of glacial acetic acid in 400ml of water, according to the Béchamp method, to yield 4-[(4-anilino-6-diethanolamino-1,3,5-triazin-2-yl)amino]-4'-aminostilbene-2,2'-disulphonic acid.

*Step 3*

To a stirred suspension of 3.6g of cyanuric chloride in 50ml of methyl ethyl ketone and 50g of ice, a solution of 13.3g of 86% 4-[(4-anilino-6-diethanolamino-1,3,5-triazin-2-yl)amino]-4'-aminostilbene-2,2'-disulphonic acid in 160g of ice-water over 30 minutes. The temperature is raised to 10°C over a period of 1 hour, the pH being maintained at 6.0-6.5 by addition of a total amount of approximately 4ml of 1M aqueous sodium carbonate solution. To the resulting suspension, 1.7g of aniline are added and the temperature raised to 30°C. After stirring for 1 hour, during which time the pH is maintained at 6.5-7.0 by addition of 1M aqueous sodium carbonate solution, a further 0.33g of aniline are added and stirring continued for a further 1 hour at 30°C. The mixture is then cooled and acidified and the product filtered to yield 4-[(4-anilino-6-diethanolamino-1,3,5-triazin-2-yl)amino]-4'-[(4-anilino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid.

*Step 4*

2g of 4-[(4-anilino-6-diethanolamino-1,3,5-triazin-2-yl)amino]-4'-[(4-anilino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid are reacted with 0.6g of aspartic acid in 25ml of water at 95°C over 4 hours, during which time the pH is maintained at 8.0-8.5 by addition of a total of 1.1g of 32% aqueous sodium hydroxide solution. The product is precipitated by addition of a mixture of ethanol and isopropanol to the reaction solution, filtered and dried to yield compound (104b).



## **Application Examples**

### **Pulp Mass Application – Examples 7-9**

To a fibre dispersion containing 2g of a mixture of 50% bleached beech and 50% bleached pine fibres of 35° SR (Schopper-Riegler) in water of 10° German hardness are added 10% of calcium carbonate filler. 0.2% of the appropriate fluorescent whitening agent, calculated as 100% active substance, are then added as an aqueous solution. After stirring for 15 minutes, 0.03% of a cationic polyacrylamide retention agent are added and handsheets formed using the Rapid-Koethen system. After drying, the CIE Whiteness and ISO Fluorescence of the sheets are recorded. The results are summarized in Table 1 below.

**Table 1**

<b>Example Nr.</b>	<b>FWA</b>	<b>CIE Whiteness</b>	<b>ISO Fluorescence</b>
7	(101)	129	19.4
8	(102)	131	20.2
9	(103)	130	20.3

### **Coating Application – Example 10**

To a coating colour having a solids content of 62% and consisting of 60% calcium carbonate and 40% clay, 0.2 parts of polyvinyl alcohol and 9 parts of SBR binder, based on the weight of the pigment, are added followed by 0.2 parts of the fluorescent whitening agent (103) of Example 3. After stirring for 15 minutes to homogenize the coating colour, a base paper free of fluorescent whitening agent is coated using a laboratory blade coater with a coating speed of 50m/min. such that a coat weight of 12g/m<sup>2</sup> results. After drying, the CIE Whiteness and Iso-fluorescence values are measured.

CIE Whiteness 95.4

Iso-fluorescence 7.1

### Water Solubility

By producing saturated solutions of the appropriate fluorescent whitening agents, the water solubilities are determined, the values being summarised in Table 2 below.

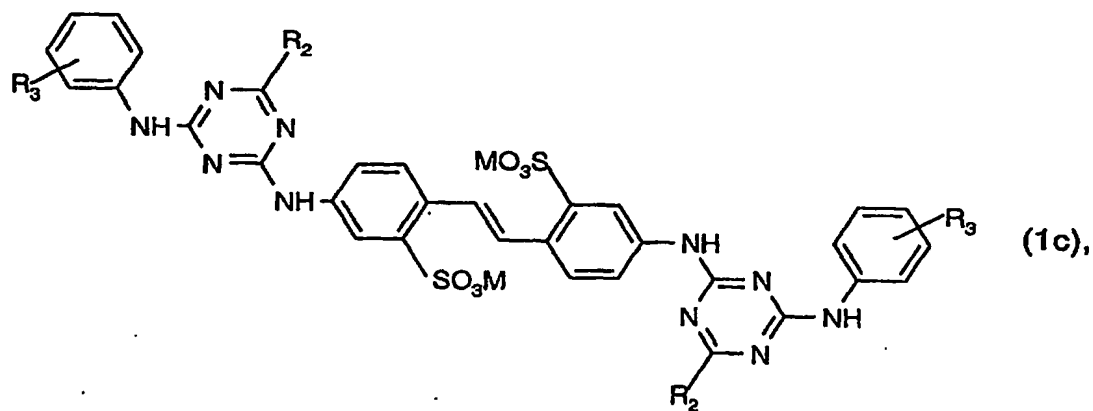
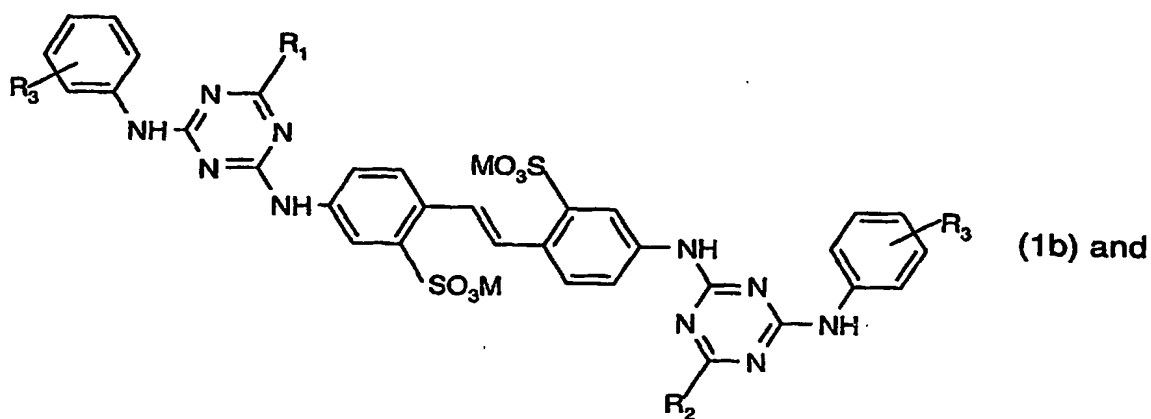
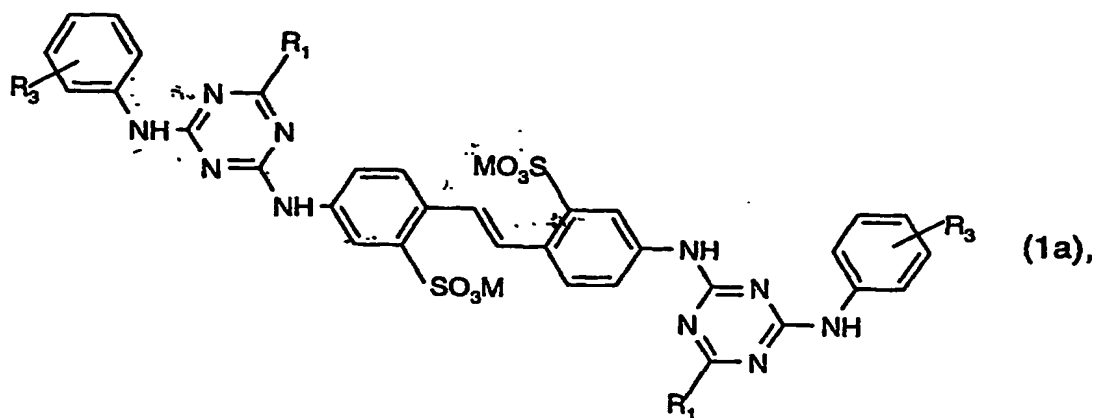
Table 2

Fluorescent Whitening Agent	Water Solubility
(101a)	3-3.5%
(101)	9%
(102)	12%
(103)	7%

The results clearly demonstrate the superior water solubility of the mixtures of the invention in comparison to one single component.

# Claims

1. A fluorescent whitening agent, which comprises a mixture of compounds of the formulae



in which

$\text{R}_1$  and  $\text{R}_2$  are different and each represents  $-\text{NH}_2$ ,  $-\text{NHC}_1\text{-C}_4\text{alkyl}$ ,  $-\text{N}(\text{C}_1\text{-C}_4\text{alkyl})_2$ ,

-NHC<sub>2</sub>-C<sub>4</sub> hydroxyalkyl, -N(C<sub>2</sub>-C<sub>4</sub> hydroxyalkyl)<sub>2</sub>, -N(C<sub>1</sub>-C<sub>4</sub>alkyl)(C<sub>2</sub>-C<sub>4</sub> hydroxyalkyl), a morpholino, piperidino or pyrrolidino residue or an amino acid or an amino acid amide residue from which a hydrogen has been removed from the amino group, each R<sub>3</sub>, independently, represents hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl or C<sub>1</sub>-C<sub>4</sub>alkoxy and M represents hydrogen, an alkali metal atom, ammonium or a cation formed from an amine.

2. A composition according to claim 1, in which R<sub>3</sub> represents hydrogen.

3. A composition according to claims 1 or 2, in which the aliphatic amino acid or amino acid amide residue is of the formula



in which each

R<sub>4</sub> and R<sub>4</sub>, independently, represent hydrogen or a group having the formula -CHR<sub>5</sub>R<sub>6</sub> in which

R<sub>5</sub> and R<sub>6</sub>, independently, are hydrogen or C<sub>1</sub>-C<sub>4</sub>alkyl optionally substituted by one or two substituents selected from the group consisting of hydroxy, thio, methylthio, amino, carboxy, sulfo, phenyl, 4-hydroxyphenyl, 3,5-diiodo-4-hydroxyphenyl, β-indolyl, β-imidazolyl and NH=C(NH<sub>2</sub>)NH-.

4. A composition according to claim 3, in which residues R<sub>1</sub> and/or R<sub>2</sub> are derived from glycine, alanine, sarcosine, serine, cysteine, phenylalanine, tyrosine (4-hydroxyphenylalanine), diiodotyrosine, tryptophan (β-indolylalanine), histidine ((β-imidazolylalanine), α-aminobutyric acid, methionine, valine (α-aminoisovaleric acid), norvaline, leucine (α-aminoisocaproic acid), isoleucine (α-amino-β-methylvaleric acid), norleucine (α-amino-n-caproic acid), arginine, ornithine (α,δ-diaminovaleric acid), lysine (α,ε-diaminocaproic acid), aspartic acid (aminosuccinic acid), glutamic acid (α-aminoglutaric acid), threonine, hydroxyglutamic acid and taurine, as well as mixtures and optical isomers thereof, or from iminodiacetic acid or from N-(propionamido)-N-(2-hydroxyethyl)amine.

5. A composition according to claims 1 or 2, in which

R<sub>1</sub> and R<sub>2</sub> represent -NHC<sub>2</sub>-C<sub>4</sub> hydroxyalkyl, -N(C<sub>2</sub>-C<sub>4</sub> hydroxyalkyl)<sub>2</sub>, -N(C<sub>1</sub>-C<sub>4</sub>alkyl)(C<sub>2</sub>-C<sub>4</sub> hydroxyalkyl), a morpholino residue or a residue derived from glycine, sarcosine, taurine, glutamic acid, aspartic acid or iminodiacetic acid.

6. A composition according to claim 5 in which

$R_1$  and  $R_2$  represent a diethanolamino, a di-(2-hydroxypropyl)amino, an N-(2-hydroxyethyl)-N-methylamino, an aspartic acid, iminodiacetic acid or a morpholino residue.

7. A composition according to any one of claims 1 to 6, in which

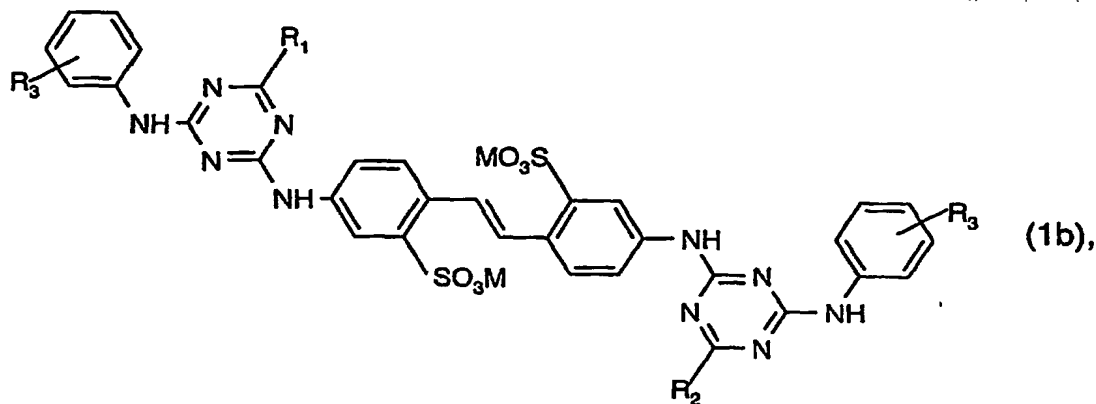
M represents hydrogen, lithium, potassium, sodium, ammonium, mono-, di-, tri- or tetra- $C_1$ - $C_4$ alkylammonium, mono-, di- or tri- $C_1$ - $C_4$ hydroxyalkylammonium or ammonium that is di- or tri-substituted with a mixture of  $C_1$ - $C_4$ alkyl and  $C_1$ - $C_4$ hydroxyalkyl groups.

8. A composition according to claim 7, in which

M represents hydrogen, potassium or sodium.

9. A process for the preparation of the compound mixture of formulae (1a), (1b) and (1c) by reacting, under known reaction conditions, cyanuric chloride, successively, in any desired sequence, with each of 4,4'-diaminostilbene-2,2'-disulphonic acid, aniline or an aniline derivative, an amino compound  $R_1H$  and an amino compound  $R_2H$ , or, alternatively a mixture of amino compounds  $R_1H$  and  $R_2H$ ,  $R_1$  and  $R_2$  being as defined in claim 1.

10. A compound of the formula



in which

$R_1$ ,  $R_2$ ,  $R_3$  and M are as defined in claim 1.

11. Use of a composition which contains water, a fluorescent whitening agent which comprises a mixture of the compounds (1a), (1b) and (1c), according to any one of claims 1 to 8, and, optionally, auxiliaries, for whitening synthetic or natural organic materials,.

12. Use according to claim 11 as optical brightening agents for paper in pulp, size-press, metering press or coating applications.

13. Paper, which has been optically brightened by the compound mixture of formulae (1a), (1b) and (1c) according to any one of claims 1 to 8.

**Abstract**

The present invention relates to a fluorescent whitening agent comprising a mixture of two symmetrically and one unsymmetrically substituted triazinylaminostilbene disulphonic acids, novel unsymmetrically substituted derivatives, a process for their preparations and use of the mixture for whitening synthetic or natural organic materials, especially paper.

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